

EFFECT OF CROPPING SYSTEMS ON HEAVY METAL DISTRIBUTION AND MERCURY FRACTIONATION IN THE WANSHAN MINING DISTRICT, CHINA: IMPLICATIONS FOR ENVIRONMENTAL MANAGEMENT

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Abstract: The authors studied the concentration of heavy metals and mercury fractionation in contaminated soil in 2 agricultural land use systems (paddy rice and dry land) at the Wanshan mercury mine in China. The average concentrations of chromium, lead, copper, nickel, and zinc were generally lower in paddy rice soil relative to corn field soil. Soil under corn field production was slightly contaminated with lead (22–100 mg/kg), copper (31–64 mg/kg), and nickel (22–76 mg/kg) and moderately contaminated with zinc (112–635 mg/kg). In both soils, correlation of these metals with the titanium concentration in the soil indicates a geogenic origin for each metal (lead, $r = 0.48$; copper, $r = 0.63$; nickel, $r = 0.47$; zinc, $r = 0.48$). The mercury and antimony concentration in soil was high under both cropping systems, and future remediation efforts should consider the potential environmental risk presented by these metals. The concentration of bioavailable mercury in soil ranged from 0.3 ng/g to 11 ng/g across the 2 cropping systems. The majority of mercury (>80%) was associated with organic matter and the residual fraction. However, soil under paddy rice production exhibited a significantly lower concentration of Fe/Mn oxide-bound mercury than that under corn field production. This may be a function of the reduction of Fe/Mn oxides in the paddy rice soil, with the subsequent release of adsorbed metals to the soil solution. Sequential change from corn field to paddy rice production, as practiced in Wanshan, should therefore be avoided. Mercury adsorbed to Fe/Mn oxides in corn field soil potentially could be released into the soil solution and be made available for biomethylation under the flooded water management conditions of a rice paddy. *Environ Toxicol Chem* 2014;33:2147–2155. © 2014 SETAC

Keywords: Potential environmental risk Hg fractionations Antimony Agricultural land use change

INTRODUCTION

Mercury (Hg) and its compounds are highly toxic and are included on the US Environmental Protection Agency's list of priority toxic pollutants [1]. The neurotoxicity of Hg has been proven, and the metal has been implicated in causing neurodegenerative diseases such as Alzheimer's disease and Parkinson's disease [2].

Both natural and human activities contribute to the presence of Hg in soil. Predominant anthropogenic sources of Hg include emissions from coal combustion, discharge of Hg-containing wastewater from industrial factories, large-scale Hg and gold (Au) mining/smelting activities, and artisanal and small-scale mining [3–6]. However, Hg is not the only metal present in land contaminated by anthropogenic activities. The heavy metals lead (Pb), antimony (Sb), copper (Cu), chromium (Cr), zinc (Zn), nickel (Ni), and thallium (Tl) are also ubiquitous in mining-affected environments, and the accumulation and transportation of these metals in the food chain will cause damage to plants, animals, and humans [7].

The Wanshan Hg mine, located in the eastern part of Guizhou province, constitutes the largest historic Hg-producing district in China. A large quantity of mine waste was produced at Wanshan between 1949 and the early 1990s [3]. Mercury contamination of the Wanshan environment has been well studied [8]. The total Hg concentration in soil ranges from 1.5 mg/kg to 790 mg/kg [3],

an upper value that is 3 orders of magnitude greater than the maximum allowable limit for Hg in Chinese agriculture soils (1.5 mg/kg) [9]. The legacy of Hg contamination across the Wanshan region clearly necessitates the remediation or management of contaminated soil. In response to this need, the government of China recently allocated a large amount of money to the future remediation of Wanshan according to Chinese environmental quality guidelines. The extent to which other metals may coexist in soil with Hg, however, has not been established. The primary Hg ore in the Wanshan mining area is cinnabar, with minor metacinnabar and elemental Hg. Minerals such as stibnite, sphalerite, and pyrite are found in association with the Hg ore, and these minerals contain a range of other heavy metals. Few efforts have been made to investigate the distribution of other heavy metals in the Hg-contaminated soils of this mining region.

Paddy rice and dry land cropping (corn and rape) are the 2 main agricultural practices in the Wanshan region, representing 6% and 3% of total land use, respectively (area). In general, rice is produced during the wet summer months, whereas vegetable crops (rape) are grown from late autumn to spring. Rape or corn is grown on paddy land after the rice harvest according to demand but is not generally on a fixed schedule. Agricultural land at Wanshan therefore experiences an alternating sequence of flooded land to dry land status each year. This integrated cropping system has the potential to affect the distribution and speciation of heavy metals in soil. Specifically, changes in soil redox can strongly influence the soil's physical and chemical characteristics. Surface coatings of iron and manganese hydrous oxides (Fe/Mn oxides) on soil particles are considered to be an

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important sink for metals in the soil [10]. Any change of soil redox may influence the chemical speciation of Fe/Mn oxides in soil and subsequently lead to the repartitioning of metals between the geochemical fractions that are present [11]. Han and Banin [12] found that cobalt (Co), vanadium (V), Ni, Zn, and Cu were transformed from a nonavailable form into a readily available form as a result of incubation of soil under the saturated conditions typical of a paddy rice environment. This transformation is the result of the release of sorbed metals from Mn and Fe oxide coatings as these surfaces are reduced [12]. As land dries with the onset of dry land cropping, however, Fe/Mn oxides will re-form, leading to a decrease in the concentration of these same metals in soil solution.

Paddy rice soil in Hg-contaminated areas is reported to have a greater concentration of methylmercury (MeHg) than dry land soils (rape or corn production) [3]. This is attributable to the bacterial methylation of bioavailable mercury in the anoxic environment, which is characteristic of a paddy field [13]. The effects that changes in soil redox caused by a sequential cropping system will have on Hg transformations in soil is poorly understood. Sequential extraction procedures have been used extensively to define the concentration of bioavailable Hg in soil. These sequential extraction procedures separate soil Hg into operationally defined groups based on chemical reactivity [14,15]. The bioavailable concentration of Hg in soil defined by sequential extraction procedures has been well correlated with concentrations of inorganic Hg in plants [16].

The present study investigated the hypothesis that an alternating sequence of paddy rice and dry land cropping will effect changes in heavy metal concentration and Hg speciation in soil. The objective of the present work was to assess the extent to which potential environmental risk at Wanshan may be induced by the cropping system used by farmers. Specifically, we investigated differences in heavy metal distribution and Hg fractionation in soil that could be induced by agricultural land use. The results of the present research are expected to assist in managing mercury pollution in this historic Hg-mining region by understanding the effect that cropping systems may have on heavy metal bioavailability.

MATERIALS AND METHODS

Soil sample collection

Soil was collected from 19 sampling locations throughout the Wanshan mining region (Figure 1). Each of these locations has been affected directly by historic Hg mining activities and represents the current dominant land use of the area. Nine locations were under paddy rice production adjacent to the Da Shui Xi River (flooded water management). Today, this river is heavily contaminated as a result of drainage from local Hg mines [17]. Ten locations were under corn field production (dry land). Each of these sampling locations was near a mercury mining shaft distributed along the margins of valleys away from the river. At each sampling site, a composite soil sample composed of 5 subsamples was collected using a stainless steel spade to 20 cm depth from an area of 2 m² (approximately 1 kg soil). All samples were collected and stored in sealed polyethylene bags to avoid cross contamination, transferred to the laboratory, freeze-dried, ground in a ceramic disc mill, and sieved to 200 mesh.

Analysis of soil physical and chemical properties

The pH of the soil was measured in deionized water at a soil-to-water ratio of 1:2.5 (w/w) using a pH meter (Hanna

Instruments). Soil texture was determined using a Malvern Mastersizer 2000 (Malvern), and the organic matter concentration was determined according to the potassium dichromate volumetric method [18]. Total carbon, total nitrogen, and total sulfur were measured directly using a PE2400-II Elemental Analyzer (PerkinElmer).

For total mercury analysis, 0.1-g to 0.2-g soil samples were digested in a water bath (95 °C) using 5 mL aqua regia and then made to a volume of 50 mL with double deionized water [19]. The concentration of Hg in the digest solution and the leachates from fractions 3, 4, and 5 were measured by cold vapor atomic absorption spectrometry using a F732-S spectrophotometer (Huaguang). The extracts from fractions 1 and 2 were determined using the dual-stage gold amalgamation method and cold vapor atomic fluorescence spectrometry using a Tekran 2500 (Tekran Instruments).

For total heavy metal determination, 0.1-g soil samples were digested by HNO₃-HF mixture (4:3, v/v) [20] in Teflon tubes at 200 °C for 48 h in an electric constant-temperature drying oven. The solution was heated until the acid was reduced to a volume of 1 mL to 2 mL and was then increased to a volume of 15 mL with 1% HNO₃. The digest solution was analyzed by Quadrupole Inductively Coupled Plasma Mass Spectrometer (ELAN DRC-e, PerkinElmer) for Tl, Pb, Sb, Cu, Cr, Zn, Ni, and Ti.

Contamination index

A contamination index (P_i) used to describe the contamination of a given toxic substance in soils was expressed by the following equation [21]

$$P_i = \frac{C_i}{X_a}$$

where C_i is the observed concentration of the substance and X_a is the noncontaminated threshold value [22]. The noncontaminated threshold values of Pb, Cu, Cr, Zn, Ni, Tl, Hg, and Sb defined by Zhang et al. [23], Ning et al. [24], and the China National Environmental Monitoring Centre [25] are 35.2 mg/kg, 26 mg/kg, 96 mg/kg, 82 mg/kg, 34 mg/kg, 0.7 mg/kg, 0.11 mg/kg, and 1.9 mg/kg, respectively. According to Chen [21], the contamination index can be classified into 4 groups: $P_i \leq 1$, no contamination; $1 < P_i \leq 2$, low contamination; $2 < P_i \leq 3$, moderate contamination; and $P_i > 3$, high contamination.

Sequential extraction procedure

A modified sequential extraction procedure based on the schemes of Tessier et al. [26] and Jeyakumar et al. [27] was used to investigate the geochemical fractionation of Hg in the soil. This methodology was limited to Hg because of the known anthropogenic contamination of this metal in the Wanshan environment. The sequential extraction procedure defined Hg as belonging to 1 of 5 chemical fractions or soil geochemical phases: soluble and exchangeable, specifically sorbed, Fe/Mn oxide-bound, organic-bound, and the residual fraction [28]. Sequential extraction was carried out with an initial weight of 1 g of sieved dry soil mixed with the relevant extractant in a 50-mL polypropylene centrifuge tube. After each step, the extracts were centrifuged at 3500 rpm, and the supernatant was separated by passing through a 0.45- μ m microfilter. The residue was washed 2 times with 8 mL of double deionized water before the next step. For the soluble and exchangeable Hg (fraction 1), the soil was extracted at room temperature for 1 h with 8 mL of 1M

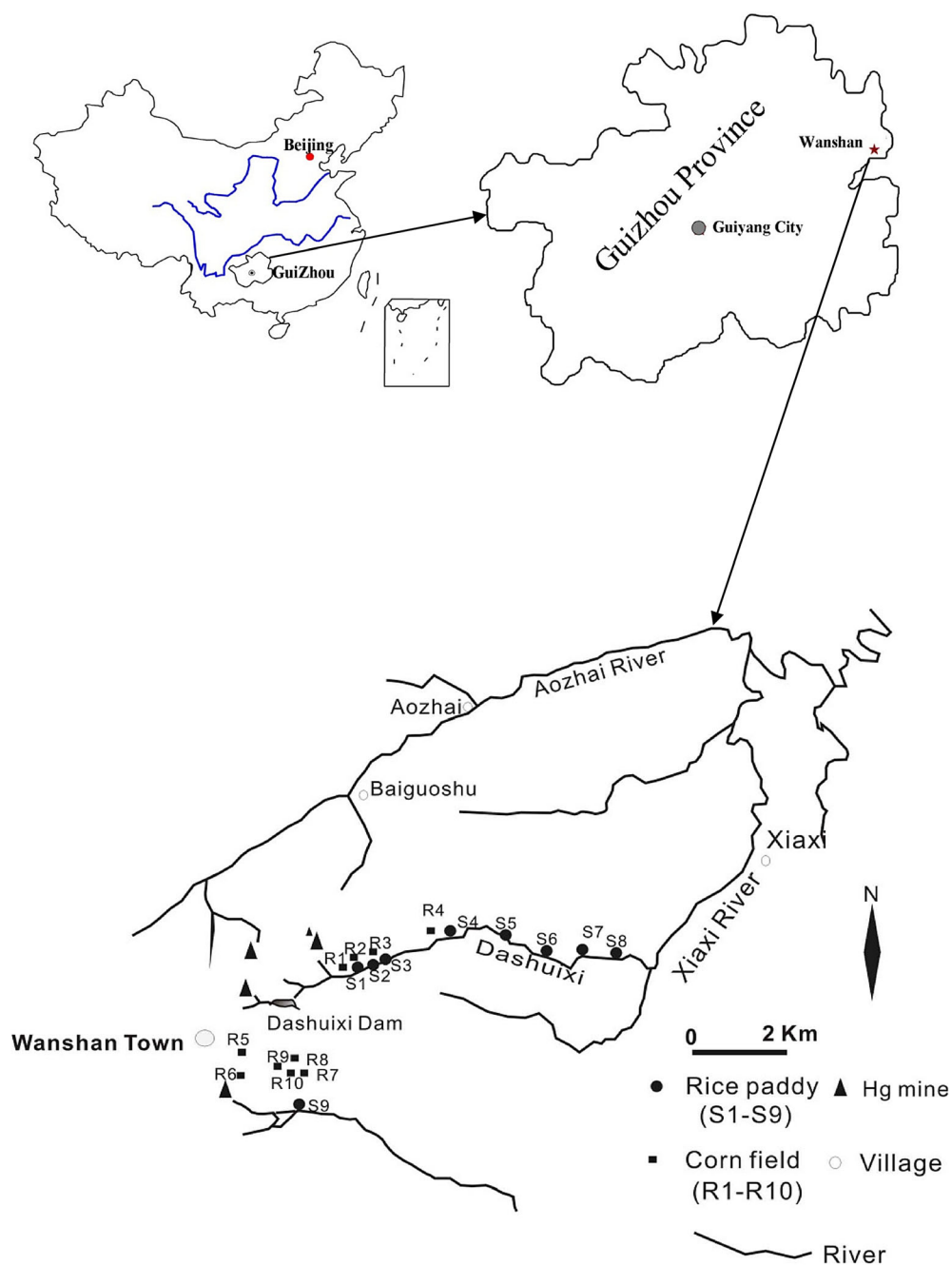


Figure 1. Location of the soil sample sites.

$\text{Mg}(\text{NO}_3)_2$ (pH7) with continuous stirring. For the specifically-sorbed Hg (fraction 2), the washed residue of fraction 1 was leached at room temperature with 8 mL of 1 M CH_3COONa (adjusted to pH5 with CH_3COOH) for 5 h with continuous stirring. For Fe/Mn oxide-bound Hg (fraction 3), the residue of fraction 2 was extracted with 20 mL of 0.4 M hydroxylamine hydrochloride ($\text{NH}_2\text{OH} \cdot \text{HCl}$) in 25% CH_3COOH (v/v) for 6 h at 96 °C in a water bath. For organic-bound Hg (fraction 4), the residue of fraction 3 was extracted with 8 mL of 30% H_2O_2 (adjusted to pH2 with HNO_3) for 2 h at 85 °C in a water bath. After 2 h, an additional 3 mL of 30% H_2O_2 was added (adjusted to pH2 with HNO_3). The temperature was maintained for another 3 h at 85 °C in a water bath. Finally, for residual Hg

(fraction 5), the residue of fraction 4 was digested with 10 mL of fresh aqua regia for 30 min at 95 °C in a water bath.

The reliability of the sequential extraction procedure method was quantified using the parameter “recovery,” which is defined as the sum of extracted Hg fractions divided by the independently determined total Hg concentration. Recovery ranged between 81% and 121% for the soil samples and was similar to that reported in previous sequential extraction procedure studies for Hg in soil [15]. There are several possible explanations for the discrepancy between the recorded recovery and the nominal value of 100%. Loss of volatile Hg species during the manipulations can result in a recovery of less than 100% [29]. Also, any uncertainty in individual chemical

measurements can also lead to a discrepancy between the actual and nominal values.

Quality control and quality assurance

Quality assurance and quality control were performed using a system of method blanks, duplicates, and certified reference materials (GBW07405 and GBW[E]070009). The average total Cu, Pb, Sb, Zn, Ni, and Cr concentrations of the soil standard GBW07405 were 133 ± 0.1 mg/kg, 468 ± 2 mg/kg, 33 ± 0.6 mg/kg, 489 ± 14 mg/kg, 38 ± 6.4 mg/kg, 111 ± 1.4 mg/kg, respectively ($n=3$), which is similar to the certified value of 166 ± 9 mg/kg, 552 ± 44 mg/kg, 35 ± 7 mg/kg, 494 ± 39 mg/kg, 40 ± 5 mg/kg, and 118 ± 10 mg/kg, respectively. The average total Hg and Ti concentrations of the soil standard GBW(E)070009 were 2.1 ± 0.1 mg/kg and 3062 ± 4 mg/kg, respectively, which is similar to the certified values of 2.2 ± 0.4 mg/kg and 4120 ± 400 mg/kg, respectively ($n=3$). The relative difference between the sample replicates was $<10\%$.

Data analysis

Statistical analyses were carried out using the software package SPSS 17.0 for Windows. Data were tested for normality and correlations among the different heavy metals using the Spearman correlation analysis (for non-normally distributed data). Significant differences were declared at $p < 0.05$ and $p < 0.01$.

RESULTS AND DISCUSSION

Soil physical and chemical characteristics

Table 1 presents the physical and chemical characteristics of the sampled soils. Soil pH varied from 5.2 to 7.8, although no clear distinction was observed between the 2 cropping systems. The Wanshan Hg mining district has abundant outcrops of limestone, which account for the generally high soil pH [3]. Soil organic matter content ranged from 1.6% to 6.7% across the 2 cropping systems. Wanshan farmers apply large amounts of farmyard manure to soil, which may explain the variable levels of organic matter content across the 2 sites. The total carbon and total nitrogen content of soil across the sampling areas did not show any significant difference between the 2 cropping systems. A significant difference was observed, however, in the total sulfur content of the soil. The sulfur content of the corn field soil was nearly 20 times higher than in the paddy rice soil ($p < 0.05$). There was no single dominant soil texture recorded in the area.

Heavy metal in soil as a function of the 2 cropping systems

The heavy metal concentration in soil under both cropping systems is shown in Table 2. In the corn field soils, with the

single exception of Cr, the average concentration of each metal exceeded the noncontaminated threshold value, especially for Zn, Sb, and Hg. These 3 metals were present at concentrations nearly 3.5 times, 19 times, and 785 times greater, respectively, than the noncontaminated threshold value. In the paddy rice soils, the average concentrations of Zn, Sb, and Hg were nearly 1.5 times, 11 times, and 524 times greater, respectively, than the noncontaminated threshold value. However, the other metals were present at a concentration similar to the noncontaminated threshold value.

The contamination index for each soil is illustrated graphically in Figure 2. For soil samples collected under paddy rice production, the contamination indexes for Cr, Pb, Tl, and Ni were at values well below 1 and for Zn and Cu at values exceeding 1. These indices suggest that paddy rice soils have not been contaminated with Pb, Tl, Cr, and Ni through anthropogenic activities. For corn field soil, the average index value for Cr was below 1; the Pb, Tl, Cu, and Ni index values were between 1 and 2; and the contamination index for Zn was greater than 3. These data indicate that Wanshan soil under corn field production is not contaminated with Cr; is slightly contaminated with Pb, Cu, Ni and Tl; and is heavily contaminated with Zn through anthropogenic activity. Both the paddy rice and corn field soil samples were contaminated heavily with Sb and Hg, as quantified by a contamination index exceeding the upper limit of 3.

Contamination of the Wanshan area with Hg is well described in literature. However, our report of significant anthropogenic Sb contamination is novel. Antimony is a nonessential element in plants, animals, and humans and can be toxic at elevated concentrations [30]. Based on the present study, the soil Sb concentration across the 2 land uses ranged from 2.6 mg/kg to 92 mg/kg. For comparison, the average concentration of Sb in soils across Guizhou Province is reported to be 2.2 mg/kg [31]. The present study's data are comparable to data obtained from other studies conducted at non-Sb mining areas. The average concentration of Sb in soil samples collected from abandoned mines in Portugal was 663 mg/kg [32]. However, the Sb concentration in Wanshan soil was generally lower than that recorded in other Sb-mining areas. Soil samples collected from the Xikuangshan Sb mining area in Hunan province, China, for example, have recorded Sb concentrations ranging from 100 mg/kg to 5050 mg/kg [33]. To the best of our knowledge, there is no Chinese environmental standard for Sb in soil. The maximum permissible Sb concentration in soil suggested by the World Health Organization is 36 mg/kg [34], and several of the Wanshan soil samples had an Sb concentration that exceeded this value. However, Oorts and Smolders [35] reported that a more accurate Sb toxicity threshold in soil was 370 mg/kg. The mobility of Sb in soil is affected by the soil pH, redox status, and

Table 1. General physicochemical parameters of soils of the 2 crops investigated in the present study

	pH	Organic matter (%)	Texture			Total C (mg/g)	Total N (mg/g)	Total S (mg/g)
			Sand (%)	Silt (%)	Clay (%)			
Cornfield ($n=10$)								
Range	5.2–7.8	1.6–6.7	14–42	26–54.0	21–47	11–49	1.4–3.9	0.2–5.9
Mean \pm SD	6.9 ± 0.7	3 ± 1.5	29.2 ± 7.2	37 ± 11	36.4 ± 10	22 ± 11	2.3 ± 0.7	1.9 ± 1.6
Paddy rice ($n=9$)								
Range	5.2–7.6	1.9–3.6	23–43	28–47	25–35	12–21	1.4–2.5	0.1–0.2
Mean \pm SD	6.3 ± 1	2.8 ± 0.6	32 ± 8	39 ± 7	29 ± 3	17 ± 2.9	1.8 ± 0.3	0.1 ± 0.1

SD = standard deviation.

Table 2. Concentrations of heavy metals in soil of the 2 crops (mg/kg; range and mean \pm standard deviation [SD]) and the relevant noncontaminated threshold values (mg/kg)

	Cr	Ni	Cu	Zn	Sb	Tl	Pb	Hg	Ti
Corn field soil ($n = 10$)									
Range	40–159	22–76	31–64	112–635	2.6–88	0.4–1.5	22–100	1.7–188	5280–7281
Mean \pm SD	86 \pm 42	43 \pm 18	45 \pm 10	283 \pm 188	35 \pm 30	0.9 \pm 0.3	51 \pm 26	90 \pm 70	6157 \pm 608
Paddy rice soil ($n = 9$)									
Range	35–139	11–68	19–55	81–272	3–92	0.4–1.1	18–37	9–222	4945–7055
Mean \pm SD	71 \pm 33	31 \pm 18	33 \pm 13	127 \pm 62	21 \pm 30	0.7 \pm 0.2	27 \pm 7	60 \pm 67	5985 \pm 789
Noncontaminated threshold values	95.9	34	26	82	1.89	0.71	35.2	0.11	—

reactive surfaces in the soil (e.g., iron oxides content) [36]. A detailed investigation of the bioavailability of Sb in Wanshan soil and the concentration of this metal in crop plants should be conducted in the future to quantify the potential for environmental risk that may be associated with Sb in soil.

The average concentration and contamination index of Cr, Ni, Cu, Zn, Hg, Sb, Tl, and Pb in the paddy rice soils were generally lower than those in the corn field soils, indicating a relatively greater degree of heavy metal contamination under corn field production than under paddy rice production. The key difference between these 2 cropping systems is the water management during crop production. Rice paddies are subject to flood irrigation, whereas land cultivated for corn production in Wanshan is not irrigated. Previous reports have shown that certain heavy metals (Cu, Pb, and Zn) in flooded or wetland soils can be lost from the surface soil profile as a result of cultivation [12,37]. Saturating the soil by flood irrigation can strongly affect soil Eh and water content [22,38], parameters that can influence the solubility of heavy metals dramatically and cause their redistribution in the soil [12,38]. Han and Banin [12] conducted a pot experiment to investigate the transformation of Ni, Cu, and Zn in soils under saturated water management and showed that each of these metals was transformed from a nonavailable to an available form as the degree of water saturation increased. These solubilized metals may be lost from the soil through uptake by the plants and harvesting or through agricultural runoff and leaching after cultivation [39].

Correlation between Ti and heavy metals in soils

Titanium can be used in geological studies as a reference for crustal materials because of its insolubility and abundance in rock and because this element is less affected by anthropogenic sources of pollution than are other heavy metals [40]. The analysis of Ti can trace the source of heavy metals in soils. A positive correlation between the concentrations of a heavy metal in soil with that of Ti indicates a geogenic origin rather than anthropogenic contamination [41]. The Spearman's correlation matrix between the Ti and heavy metal concentration in the collected soils is presented in Table 3. With the exception of Sb, Cr, and Hg, the metals Ni, Cu, Zn, Tl, and Pb are significantly correlated with Ti. Correlation suggests that the loading of these metals to soil may be through geogenic processes, most likely the natural weathering of rocks over time. In contrast, the Hg and Sb concentration in soil under both land uses is not correlated with Ti. This lack of correlation supports the hypothesis that the presence of these metals in Wanshan soil is a function of anthropogenic contamination. The Wanshan Hg deposit is located in a large natural circum-Pacific mercuriferous belt. Elements such as S, Sb, Tl, and As generally are associated with Hg in the mercury-bearing minerals of this belt. The occurrence of antimony-bearing minerals such as stibnite has been recorded in the Wanshan Hg deposit [42], and the mining and

refining of Hg may have released Sb-containing wastes into the environment. As a result of the present study, we define Sb as well as Hg as having the potential to cause environmental risk in the Wanshan area.

The distribution of Hg fractionations in soil

In any environmental consideration of heavy metal in soil, the greatest concern is related to the potential for transfer of metal from soil to plants, which may enter the food chain and pose a health risk to humans. Risk in this context can be better understood through use of a sequential extraction procedure, which estimates the concentration of bioavailable metal in soil. The 2 candidates for sequential extraction procedure study in the Wanshan soil are Hg and Sb, based on their contamination status reported in the present study. Of these 2, Hg has been studied extensively, and the presence of this metal in soil is the primary environmental concern for the Wanshan region. Bioavailable Hg is defined as that associated with the soluble and exchangeable (fraction 1) and specifically sorbed (fraction 2) geochemical fractions in soil [43]. A sequential extraction procedure for Sb is not described in the present study. The methodology for a reliable Sb sequential extraction procedure is being developed as a result of the present study's findings and will be described in future publications.

The bioavailable Hg concentration in the corn field and paddy rice soils ranged from 0.3 ng/g to 11 ng/g (Table 4) and was similar to results Wang et al. [15] obtained for Wanshan soil. There was no difference in bioavailable concentration as a function of cropping system. The average bioavailable concentration of Hg in the Wanshan soil samples was lower than that reported for an uncontaminated background soil in China (0.04 mg/kg) collected from the Qiliangqiao Natural Beauty Spot (~70 km from Wanshan) [44]. In contrast, the reported bioavailable Hg concentration in soil collected from the Almadén Hg mine in Spain is 0.2 mg/kg to 8 mg/kg [45], 2 to 3 orders of magnitude greater than that for Wanshan. Huang et al. [46] collected several soil and rice samples from an industrial region in the Yangtze River Delta area of China and correlated the concentration of bioavailable Hg in soil with the total Hg concentration in rice. For a reported bioavailable Hg concentration range from 31 ng/g to 35 ng/g in soil, the average concentration of Hg in rice was well below the maximum allowable Hg content in foodstuffs established by the Chinese government. We therefore propose that the very low bioavailable Hg concentrations recorded for Wanshan soil represent a low-level risk to food safety for the cropping systems analyzed at the time of the present study. However, the implications of the change between flooded and dry land water management can be considered further as follows.

Soil Hg associated with fraction 3 was significantly greater than that associated with fractions 1 and 2, and a significant

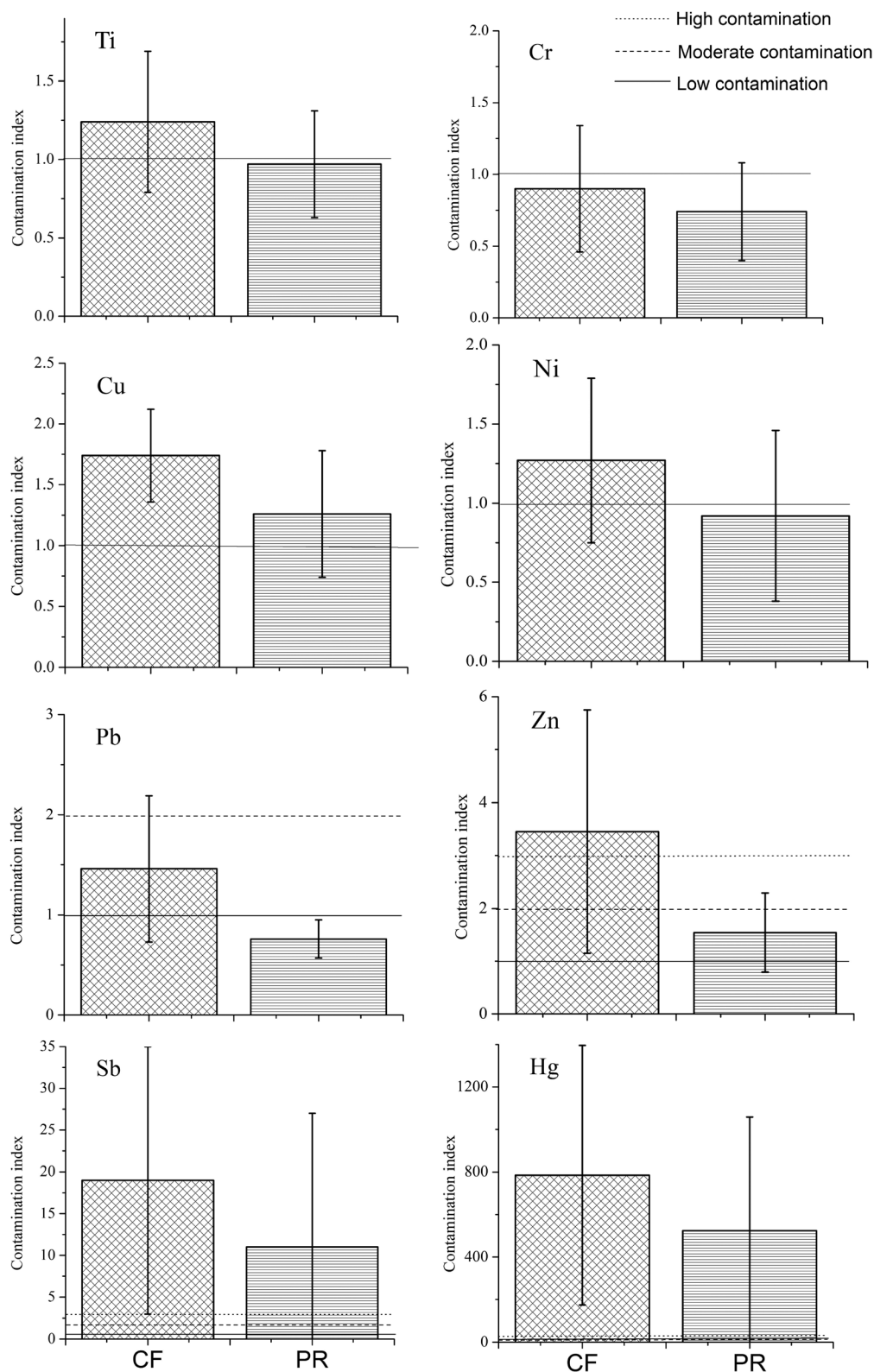


Figure 2. The contamination index of heavy metals in soil at the Wanshan mining area collected under paddy rice (PR; $n=9$) and corn field (CF; $n=10$) production. Bars denote the standard deviation from the mean of replicates.

difference between the fraction 3 concentrations as a function of cropping system was observed. For the paddy rice soils, the concentration of Hg associated with fraction 3 ranged from 0.03 mg/kg to 0.86 mg/kg. In contrast, in the corn field soils, the concentration ranged from 5 mg/kg to 36 mg/kg (Table 4).

A difference in the oxidation status of Fe and Mn as a function of the 2 land uses can be expected based on the water management conditions employed for crop production. We propose that the observed variance in the concentration of Hg associated with Fe/Mn oxides can be explained through the reduction of oxides

Table 3. Spearman's correlation matrix, giving the linear correlation coefficients (r) among the heavy metal concentrations in soil ($n = 19$)

	Ni	Cu	Zn	Sb	Tl	Pb	Ti	Hg
Cr	0.83**	0.45	0.23	0.67**	0.65**	0.40	0.28	0.34
Ni		0.73**	0.64**	0.73**	0.73**	0.60**	0.47*	0.34
Cu			0.72**	0.49*	0.86**	0.69**	0.63**	0.39
Zn				0.47*	0.44	0.79**	0.48*	0.32
Sb					0.58*	0.57*	0.23	0.81**
Tl						0.64**	0.68**	0.43
Pb							0.48*	0.42
Ti								0.26

* $p < 0.05$.
 ** $p < 0.01$.

under the anoxic conditions prevalent for paddy rice soil [11]. Reduction of soil oxides would subsequently release any sorbed metal into soil solution. Similar results have been reported in previous studies. For example, Zhang et al. [47] investigated the fractionation of Hg in soil collected from an industrial region in southern China under both flooded and dry land use. Their results indicated that the average concentration of Hg bound to Fe/Mn oxides in the paddy rice soil was 0.6 mg/kg, whereas that in the dry land soil was 3.9 mg/kg.

Compared with fractions 1, 2, and 3, organic-bound Hg is considered, in general, to have limited bioavailability in soil and to present low environmental risk [16]. In the present study, the concentration of Hg associated with organic matter was similar under both paddy rice production (4–57 mg/kg) and corn field production (12–60 mg/kg). The concentration of Hg associated with the soil residual fraction ranged from 4 mg/kg to 136 mg/kg and from 3 mg/kg to 184 mg/kg for paddy rice and corn field, respectively, and accounted for the majority of Hg in the soil under both crops. Trace elements associated with the soil residual fraction are those that are combined with primary or secondary minerals and are often components of a crystal structure. Mercury in this phase also has limited bioavailability and therefore presents low environmental risk.

Land management recommendations

The Wanshan soil investigated in the present study under both paddy rice and corn field production shows evidence of anthropogenic contamination with Hg and Sb. The presence of these contaminants may present environmental risk, and an appropriate remediation or management plan should be enacted to mitigate this risk where it is apparent. Although soil under corn field production was slightly contaminated with Zn, Pb, Ni, and Cu, these metals are likely to be present through geogenic origin, and remediation likely is not necessary. Efforts to remediate contaminated soil at Wanshan have been initiated [15,48]. However, the focus of these efforts has been to

remediate Hg only. Future efforts should consider both Hg and Sb fully.

The results of the present study indicate that each change from cornfield to paddy rice production may result in a period of increased environmental risk. Each change in land use may lead to increased mobility of heavy metals because Fe/Mn oxides are reduced with the onset of paddy rice flood irrigation. In the present study, Hg bound to Fe/Mn oxides in soil under corn production represented a high proportion of total Hg (0.3–13%). We propose that Hg associated with Fe/Mn oxides in corn field soil could be released to the soil solution under the described scenario of land use change. This soluble Hg could then be available for uptake or for methylation by bacteria in the paddy rice soil environment [49], or it may be leached. There was, however, no significant difference in the concentration of bioavailable metal in soil between the 2 crops. We therefore propose that Hg released from Fe/Mn oxides is removed rapidly from the soil solution by these same 3 pathways (uptake, methylation, or leaching). Based on this suspected risk, we believe that the changing geochemistry of Hg associated with each cropping system transition, and its accumulation in crops as a function of change, should be investigated in future research.

Antimony may represent a previously unknown or underestimated environmental risk throughout the Wanshan region, and this risk should be considered further in the context of the cropping system employed. Metal oxides and hydroxides are also important for retaining Sb in soil. Mitsunobu et al. [49] reported that the main host phase of both Sb and As in soil was Fe(III) hydroxide. Antimony is sorbed preferentially onto Fe oxides in soil [50] and Mn oxides in lake sediments [51]. Tong et al. [52] reported the use of a sequential extraction method to study the fractionation of Sb in a Sb-containing soil collected from the Lengshuijiang Sb mine in Hunan province, China, and showed that Sb associated with Fe/Mn oxides represented 30% and 51% of total Sb (up to 55 mg/kg) at 0 cm to 20 cm and 20 cm to 40 cm soil depth, respectively. Similarly,

Table 4. Concentration of Hg associated with each soil's geochemical fraction under paddy rice and corn field production (mg/kg; mean \pm standard deviation)^a

	Soluble and exchangeable Hg	Specifically sorbed Hg	Fe/Mn oxide bound Hg	Organic bound Hg	Residual Hg	Total Hg by summation of each fraction	Total Hg by single digestion
Paddy rice ($n = 9$)	0.001 \pm 0.002 (0.005 \pm 0.005)	0.002 \pm 0.002 (0.01 \pm 0.01)	0.2 \pm 0.28 (0.5 \pm 0.5)	15 \pm 19 (25 \pm 16)	37 \pm 43 (74 \pm 16)	56 \pm 60	60 \pm 67
Corn field ($n = 10$)	0.002 \pm 0.003 (0.003 \pm 0.003)	0.004 \pm 0.009 (0.01 \pm 0.01)	6.2 \pm 10.6 (12 \pm 13)	23 \pm 20 (32 \pm 19)	64 \pm 71 (56 \pm 27)	93 \pm 79	90 \pm 70

^aThe data in the parentheses indicate each fraction, representing the percentage of total Hg.

Tighe and Lockwood [53] found that Sb associated with noncrystalline Fe and Al hydroxides represented 30% to 47% of the total Sb concentration in soil (27 mg/kg). Development of a sequential extraction procedure for Sb in Wanshan soil is a target for future research. Flood irrigation of soil may increase bioavailability of Sb and leaching as the metal desorbs from reduced Fe/Mn oxides. In general, pentavalent and trivalent Sb are the 2 main forms of inorganic Sb in soil. Antimony in the trivalent state is more toxic and mobile than pentavalent Sb [54]. In contaminated soil at Sb mining sites, pentavalent Sb is the predominant speciation, representing more than 90% of total Sb in soil [55]. In paddy fields, however, pentavalent Sb may be reduced to the trivalent state [54]. Therefore, any transition from corn field to paddy rice at Wanshan may increase the mobility and toxicity of Sb in soil and pose a period of increased environmental risk. The bioavailability of Sb and its accumulation in the food chain as a function of cropping system change should be assessed fully in future environmental studies conducted in the Wanshan mining district.

CONCLUSIONS

Wanshan soils are contaminated with Hg and Sb. Remediation protocols currently being enacted for Hg-contaminated soil should therefore also consider Sb. Soils under corn production show a higher concentration of heavy metals than soils under paddy rice production, but this is associated with the differing redox status of the soils rather than a differential history of contamination. Metals in the paddy rice soil may have desorbed from Fe/Mn oxides and leached over time. The sequential extraction protocol adopted for the present study showed that the concentration of bioavailable Hg currently presents limited environmental risk under both cropping systems. A major difference was observed, however, in the concentration of Hg adsorbed to Fe/Mn oxides in soil between the 2 systems, and we propose that Hg associated with this fraction represents potential future environmental risk. A greater concentration of Hg associated with Fe/Mn oxides was found in the cornfield soils than in the paddy rice soils, and this Hg could potentially be released to soil solution as a consequence of future land-use change. Our results should be considered during agricultural land use planning in the Wanshan mining district. Where land under corn production is changed to paddy rice production, oxide-bound Hg may desorb as the oxides reduce under the flooded water management system. Such land use change could potentially lead to a short-term increase in the concentration of bioavailable Hg in soil solution, and this fraction of metal would be available for biomethylation. To prevent the possible transfer of MeHg into future rice crops in the Wanshan area, the current practice of alternating crop types may need to be avoided.

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REFERENCES

- Agency for Toxic Substances and Disease Registry, Priority List of Hazardous Substances. [cited 2014 June 9]. Available from: <http://www.atsdr.cdc.gov/SPL/index.html>.
- Mutter J, Naumann J, Sadaghiani C, Walach H, Drasch G. 2004. Amalgam studies: Disregarding basic principles of mercury toxicity. *Int J Hyg Environ Heal* 207:391–397.
- Qiu GL, Feng XB, Wang SF, Shang LH. 2005. Mercury and methylmercury in riparian soil, sediments, mine-waste calcines, and moss from abandoned Hg mines in east Guizhou province, southwestern China. *Appl Geochem* 20:627–638.
- Feng XB, Dai QJ, Qiu GL, Li GH, He LR, Wang DY. 2006. Gold mining related mercury contamination in Tongguan, Shaanxi Province, PR China. *Appl Geochem* 21:1955–1968.
- Li P, Feng XB, Shang LH, Qiu GL, Meng B, Liang P, Zhang H. 2008. Mercury pollution from artisanal mercury mining in Tongren, Guizhou, China. *Appl Geochem* 23:2055–2064.
- Yang X, Wang L. 2008. Spatial analysis and hazard assessment of mercury in soil around the coal-fired power plant: A case study from the city of Baoji, China. *Environ Geol* 53:1381–1388.
- Adriano DC. 2001. *Trace Elements in Terrestrial Environments: Biogeochemistry, Bioavailability, and Risks of Metals*. Springer, New York, NY, USA.
- Feng X, Qiu G. 2008. Mercury pollution in Guizhou, Southwestern China—An overview. *Sci Total Environ* 400:227–237.
- Chinese National Environment Protect Agency. 1995. Environmental quality standard for soils. Publication GB15618-1995. Beijing, China (in Chinese).
- Campbell PGC, Lewis AG, Chapman PM, Crowder AA, Fletcher WK, Imber B, Louma SN, Stokes PM, Winfrey M. 1998. *Biologically Available Metals in Sediments*. Publication 27694. National Research Council of Canada, Ottawa, ON.
- Han F, Banin A. 1996. Solid-phase manganese fractionation changes in saturated arid-zone soils: Pathways and kinetics. *Soil Sci Soc Am J* 60:1072–1072.
- Han F, Banin A. 2000. Long-term transformations of cadmium, cobalt, copper, nickel, zinc, vanadium, manganese, and iron in arid-zone soils under saturated condition. *Commun Soil Sci Plant Anal* 31:943–957.
- Hsu-Kim H, Kucharzyk KH, Zhang T, Deshusses MA. 2013. Mechanisms regulating mercury bioavailability for methylating microorganisms in the aquatic environment: A critical review. *Environ Sci Technol* 47:2441–2456.
- Rubio R, Rauret G. 1996. Validation of the methods for heavy metal speciation in soils and sediments. *J Radioanal Nucl Chem* 208:529–540.
- Wang JX, Feng XB, Anderson CWN, Qiu G, Ping L, Bao ZD. 2011. Ammonium thiosulphate enhanced phytoextraction from mercury contaminated soil—Results from a greenhouse study. *J Hazard Mater* 186:119–127.
- Zagury GJ, Neculita CM, Bastien C, Deschenes L. 2006. Mercury fraction, bioavailability, and ecotoxicity in highly contamination soils from chlor-alkali plants. *Environ Toxicol Chem* 25:1138–1147.
- Zhang H, Feng XB, Larssenc T, Shang LH, Vogt RD, Rothenberga SE, Li P, Zhang H, Lin Y. 2010. Fractionation, distribution and transport of mercury in rivers and tributaries around Wanshan Hg mining district, Guizhou province, southwestern China: Part 1—Total mercury. *Appl Geochem* 25:633–641.
- Lu R. 2000. *Chemical Analysis Method of Agricultural Soil*. China Agricultural Science Press, Beijing China (in Chinese).
- Remy S, Prudent P, Probst JL. 2006. Mercury speciation in soils of the industrialised Thur River catchment (Alsace, France). *Appl Geochem* 21:1855–1867.
- Voica C, Dehelean A, Iordache A, Geana I. 2012. Method validation for determination of metals in soils by ICP-MS. *Romanian Reports in Physics* 64:221–231.
- Chen HM. 2005. *Environmental Soil Science*. Science Press, Beijing China (in Chinese).
- Bai J, Yang Z, Cui B, Gao H, Ding Q. 2010. Some heavy metals distribution in wetland soils under different land use types along a typical plateau lake, China. *Soil Tillage Res* 106:344–348.
- Zhang HQ, Lin SX, Lin CH. 2011. The content characteristics of soil heavy metals and regional differences study. *Environmental Monitoring in China* 27:88–91.
- Ning XB, Xiang WH, Fang X, Yan WD, Deng XW. 2009. Heavy metal concentrations and pollution assessment of limestone forests in Huaxi district, Guiyang City. *Acta Ecologica Sinica* 29:2169–2176.
- China National Environmental Monitoring Centre. 1990. *Background Value of Soil Elements in China*. China Environmental Science Press, Beijing, China (in Chinese).
- Tessier A, Campbell PGC, Bisson M. 1979. Sequential extraction procedure for the speciation of particulate trace metals. *Anal Chem* 51:844–851.
- Jeyakumar P, Loganathan P, Sivakumaran S, Anderson CWN, McLaren RG. 2008. Copper and zinc spiking of biosolids: Effect of incubation period on metal fractionation and speciation and microbial activity. *Environ Chem* 5:347–354.
- Issaro N, Abi-Ghanem C, Bermond A. 2009. Fractionation studies of mercury in soils and sediments: A review of the chemical reagents used for mercury extraction. *Anal Chim Acta* 631:1–12.

29. Neculita CM, Zagury GJ, Deschênes L. 2005. Mercury speciation in highly contaminated soils from chlor-alkali plants using chemical extractions. *J Environ Qual* 34:255–262.
30. Amereih S, Meisel T, Kahr E, Wegscheider W. 2005. Speciation analysis of inorganic antimony in soil using HPLC-ID-ICP-MS. *Anal Bioanal Chem* 383:1052–1059.
31. He MC, Wang XP, Wu FC, Fu ZY. 2012. Antimony pollution in China. *Sci Total Environ* 421–422:41–50.
32. Pratasa J, Prasad MNV, Freitas H, Condea L. 2005. Plants growing in abandoned mines of Portugal are useful for biogeochemical exploration of arsenic, antimony, tungsten and mine reclamation. *J Geochem Explor* 85:99–107.
33. Wang XQ, He MC, Xie J, Xi JH, Lu XF. 2010. Heavy metal pollution of the world's largest antimony mine-affected agricultural soils in Hunan province (China). *J Soils Sediments* 10:827–837.
34. Chang AC, Pan GX, Page AL, Asano T. 2002. *Developing Human Health-related Chemical Guidelines for Reclaimed Waster and Sewage Sludge Applications in Agriculture*. World Health Organization, Geneva, Switzerland.
35. Oorts K, Smolders E. 2009. Ecological threshold concentrations for antimony in water and soil. *Environ Chem* 6:116–121.
36. Leuz AK, Mönch H, Johnson A. 2006. Sorption of Sb(III) and Sb(V) to goethite: Influence on Sb(III) oxidation and mobilization. *Environ Sci Technol* 40:7277–7282.
37. Panichayapichet P, Nitisoravut S, Simachaya W. 2007. Spatial distribution and transport of heavy metals in soil, ponded-surface water and grass in a Pb-contaminated watershed as related to land-use practices. *Environ Monit Assess* 135:181–193.
38. Han F, Kingery WL, Hargreaves JE, Walker TW. 2007. Effects of land uses on solid-phase distribution of micronutrients in selected vertisols of the Mississippi River Delta. *Geoderma* 142:96–103.
39. Liu R. 2003. The study of mercury behavior in mire wetlands. PhD Thesis. Northeast Institute of Geography and Agricultural Ecology, Chinese Academy of Sciences, China.
40. Rahn KA. 1976. The chemical composition of the atmospheric aerosol. Technical Report. Graduate school of oceanography University of Rhode Island, Kingston, Rhode Island.
41. Norra S, Schleicher N, Stüben D, Chai F, Chen Y, Wang S. 2010. Assessment of aerosol concentration sampled at five sites in Beijing from 2005 till 2007. In Rauch S, Morrison GM, Monzón A, (eds.). *Highway and Urban Environment. Alliance for Sustainability Book Series*, Vol. 17. Springer, Heidelberg, Germany, pp. 133–140.
42. Hua YF. 1985. A study on the behavior of mercury in weathering environment in Wanshan district. *Chinese Journal of Geochemistry* 4:325–334.
43. Wallschläger D, Desai MVM, Spengler M, Wilken RD. 1998. Mercury speciation in floodplain soils and sediments along a contaminated river transect. *J Environ Qual* 27:1034–1044.
44. Li YH, Yang LS, Ji YF, Sun HF, Wang WY. 2009. Quantification and fractionation of mercury in soils from the Chatian mercury mining deposit, southwestern China. *Environ Geochem Health* 31:617–628.
45. Millán R, Gamarra R, Schmid T, Sierra MJ, Quejido AJ, Sánchez DM, Cardona AI, Fernández M, Vera R. 2006. Mercury content in vegetation and soils of the Almadén mining area (Spain). *Sci Total Environ* 368: 79–87.
46. Huang B, Wang M, Yan LX, Sun WX, Zhao YC, Shi XZ, Weindorf DC. 2011. Accumulation, transfer, and environmental risk of soil mercury in a rapidly industrializing region of the Yangtze River Delta, China. *J Soils Sediments* 11:607–618.
47. Zhang MK, Fu JL, Gu GP, Huang CY. 2006. Chemical forms, transformation and adsorption of mercury in the soils of the Changjiang Delta and Zhujiang Delta. *J Safety Environ* 6:1–5 (in Chinese).
48. Wang JX, Feng XB, Anderson CWN, Wang H, Zheng LR, Hu TD. 2012. Implications of mercury speciation in thiosulfate treated plants. *Environ Sci Technol* 46:5361–5368.
49. Mitsunobu S, Harada T, Takahashi Y. 2006. Comparison of antimony behavior with that of arsenic under various soil redox conditions. *Environ Sci Technol* 40:7270–7276.
50. Denys S, Tack K, Caboche J, Delalain P. 2009. Bioaccessibility, solid phase distribution, and speciation of Sb in soils and in digestive fluids. *Chemosphere* 74:711–716.
51. Müller B, Granina L, Schaller T, Ulrich A, Wehrli B. 2002. P, As, Sb, Mo, and other elements in sedimentary Fe/Mn layers of Lake Baikal. *Environ Sci Technol* 36:411–420.
52. Tong F, Li G, Yang W, Shi W. 2011. Study on the effect of amendment on Sb form and bioavailability in antimony mine area. *China Agricultural Science Bulletin* 27:25–30 (in Chinese).
53. Tighe M, Lockwood P. 2007. Importance of noncrystalline hydroxide phases in sequential extractions to fractionate antimony in acid soils. *Commun Soil Sci Plant Anal* 38:1487–1501.
54. Wilson SC, Lockwood PV, Ashley PM, Tighe M. 2010. The chemistry and behaviour of antimony in the soil environment with comparisons to arsenic: A critical review. *Environ Pollut* 158:1169–1181.
55. He MC, Yun Y. 2003. The speciation and bioavailability of antimony in the soil near antimony mine area. *Environ Chem* 22:126–130.